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Synthesis, characterization and electrochromic properties of a conducting copolymer of pyrrole functionalized polystyrene with pyrrole

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Abstract

A well-defined polystyrene (PSt) based polymer containing at one end-chain 3,5-dibromobenzene moiety, prepared by atom transfer radical polymerization (ATRP), was modified in two reaction steps. First one constitutes a Suzuki coupling reaction between aromatic dibromine functional polymer and 3-aminophenylboronic acid, when a diamino-containing intermediate was obtained. The second step is a condensation reaction between the diamino functional polystyrene and 2-pyrrole aldehyde. Thus, a polymer containing a conjugated sequence having pyrollyl groups at the extremities was synthesized. The presence of oxidable pyrrole groups in the structure of the polymer permitted further electropolymerization. The structures of intermediate polymers were analyzed by spectral methods (^{1}H NMR, FTIR). Electrochemical copolymerization of pyrrole functionalized polymer (PStPy) with pyrrole was carried out in acetonitrile (ACN)-tetrabutylammonium tetrafluoroborate (TBAFB) solvent electrolyte couple. Characterization of the resulting copolymer were performed via Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), scanning electron microscopy (SEM), spectroelectrochemical analysis, and kinetic study. Spectroelectrochemical analysis show that the copolymer of PStPy with Py has an electronic band gap (due to π–π^* transition) of 2.4 eV at 393 nm, with a yellow color in the fully reduced form and a blue color in the fully oxidized form. Via kinetic studies, the optical contrast $\%\Delta T$ was found to be 20% for P(PStPy-*co*-Py). Results showed that the time required to reach 95% of the ultimate T was 1.7 s for the P(PStPy-*co*-Py).
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Keywords: Coupling processes; Electrochemical polymerization; Conducting polymers

1. Introduction

Recently, conducting polymers have received a great interest because of their wide range of practical applications in several areas such as rechargeable batteries [1,2], sensors [3,4], capacitors [5,6], membranes [7], light emitting diodes [8,9], optical displays [10,11], electrochromic devices [12], gas separation membranes [13], enzyme immobilization matrices [14,15].

Synthesis of conducting graft and block copolymers were one of the effective ways to improve poor properties of conducting polymers. The addition of an appropriate functional group to a conventional polymer is another way to impart new properties to conducting polymers.

A number of techniques for the preparation of polymers with desired end groups have been developed. Living polymerization is widely used polymerization technique to synthesize polymers with desired structure. Living polymerizations are chain growth reactions that proceed in the absence of irreversible chain transfer and chain termination. The final average molecular weight of the polymer can be adjusted by varying the initial monomer/initiator ratio, while maintaining a narrow molecular weight distribution ($M_w/M_n < 1.5$) [16]. Hence, polymers can be end-functionalized and block copolymerized with other monomers. Thus, it has opened new pathways to create many new materials with vastly differing properties by varying the topology of the polymer

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(comb, star, dendritic, etc.), the composition/architecture of the polymer (random, periodic, graft, etc.), or the functional groups at various sites of the polymer (end, center, side) [17]. ATRP, introduced by Matyjaszewski [18,19], has been proven to be effective for a wide range of monomers and appears to be a powerful tool for the polymer chemists, providing new possibilities in structural and architectural design and allowing the development of new products with monomers currently available.

Telechelic polymers and macromonomers can be used as cross-linkers, chain extenders, and precursors for block and graft copolymers. Various macromolecular architectures obtained by the reactions of telechelics and macromonomers have recently been reviewed [20,21]. We have recently proposed α,ω-telechelics via combination of atom transfer radical polymerization (ATRP) and coupling (ATRC) processes [22]. Also in our earlier works we reported the synthesis of polyphenylenes (PPs) with different architectures [23,24], mictoarm star copolymers [25], benzoxazine functional macromonomers [26] and mid-or end-chain functional telechelics [27] starting from ATRP in combination with cross-coupling processes.

The synthesis of new conjugated polymers by functionalizing precursor molecules is an attractive way to tailor both the optical and electronic characteristics of these materials. This strategy has been used mostly to find new polythiophene, polypyrrole derivatives [28] due to their suitable electronic properties associated with environmental stability and the relative ease of modifying the monomer structure [29].

The objective of this study is to attach pyrrole groups onto a conventional styrene polymer and to synthesize conducting polymers, by electrochemical polymerization methods, with improved optical properties. Polypyrrole itself reveals rather poor properties in terms of electrochromic behaviours [30]. It is common that further enhancement by doping and sensitizing with various dyes is required for good optical properties [31,32]. For this purpose, an amino-functionalized polymer was synthesized by successive ATRP and Suzuki coupling [33] and pyrrole moieties were further introduced through condensation reaction of amino groups with appropriate aldehyde compound. The resultant pyrrole functionalized polymer (PStPy) was copolymerized with pyrrole (Py). The copolymer of P(PStPy-*co*-Py) was characterized by Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM). Moreover, the spectroelectrochemical and electrochromic properties of the copolymer of PStPy with Py, P(PStPy-*co*-Py), were investigated.

2. Experimental

2.1. Materials

3-Aminophenylboronic acid hemisulfate (Acros), *p*-toluene sulfonic acid (Fluka), 2-pyrrole carboxaldehyde (Fluka), were used as received. The comonomer pyrrole (Py) (Aldrich) was distilled prior to use. The electrolysis solvents, acetonitrile (ACN) (Merck), and dichloromethane (DM) (Merck) were used without further purification. The supporting electrolytes, tetrebutylammonium tetrafluoroborate (TBAFB) (Aldrich), sodium perchlorate ($NaClO_4$) (Aldrich) and lithium perchlorate ($LiClO_4$) (Aldrich) were used as received.

2.2. Equipment

^{1}H NMR spectra were recorded in $CDCl_3$ with tetramethylsilane, using a Bruker AC250 (250.133 and 62.860 MHz, respectively). FTIR spectra of $PStNH_2$, PStPy and P[PStPy-*co*-Py] were recorded on Perkin–Elmer FTIR spectrum one spectrometer, where samples were dispersed in KBr.

Spectroelectrochemical and kinetic studies were carried out on Solartron 1285 potentiostat/galvanostat and a HP8453A UV–vis spectrophotometer. Colorimetry measurements were acquired by a Coloreye XTH Spectrophotometer (GretagMacbeth). Thermal behavior of the samples was researched via a Du Pont 2000 differential scanning calorimetry under N_2 atmosphere. Scanning electron microscopy (SEM) studies were performed by JEOL JSM-6400.

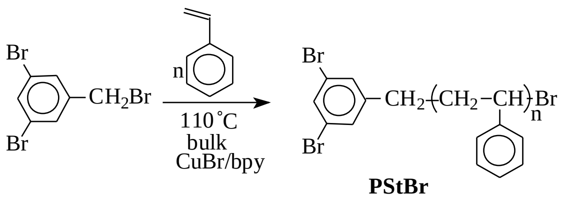
2.3. Synthesis of PStBr

PSt based polymer containing at one end-chain 3,5-dibromobenzene moiety (PStBr) was prepared by atom transfer radical polymerization (ATRP) of using as initiator 1,3-dibromo-5-(bromomethyl)benzene as shown in Scheme 1 and was reported elsewhere [24] $M_{n,GPC}=2550$, $M_w/M_n=1.25$, $M_{n,HNMR}=2500$.

2.4. Suzuki coupling reaction between PStBr and 3-aminophenyl boronic acid

A 100 mL three-necked round bottom flask equipped with a condenser, a rubber septum, a nitrogen inlet–outlet and a magnetic stirrer was charged with 10 mL, 1 M $NaHCO_3$ aqueous solution and 15 mL THF. Solvents were previously bubbled with nitrogen over a period of 30 min and the mixture was refluxed under nitrogen for 4 h.

A 20 mL three-necked round bottom flask equipped in the same way as the previous one was charged under inert atmosphere with 0.208 mmol of polymer PStBr, 0.174 g (1.04 mmol) 3-aminophenylboronic acid hemisulfate and 0.01 g (0.008 mmol) of $Pd(PPh_3)_4$. The solvent mixture (4 mL) was introduced with a syringe through the septum. The mixture was refluxed under nitrogen for 4 days,



Scheme 1. Synthesis of PStBr.

maintaining vigorous stirring and with the exclusion of oxygen and light. The amino-functionalized polymer PStNH$_2$ was separated by precipitation in methanol, filtrated, washed several times with water for the removal of inorganic salts and dried. Further purification was performed by passing the polymers through a silica gel column using THF as eluent and reprecipitated in methanol.

2.5. Synthesis of PstPy by condensation reaction of PStNH$_2$ with 2-pyrrole aldehyde

In a 25 mL three-necked round-bottom flask equipped with a Dean–Stark trap connected to a condenser, a nitrogen inlet–outlet and a magnetic stirrer were introduced 0.6 mmol of amino-functionalized polymer PStNH$_2$ and 3 mmol of 2-pyrole aldehyde in 7 mL toluene. Catalytic amounts of *p*-toluenesulphonic acid were added. The reaction mixture was refluxed for 24 h. After reflux, the polymer was precipitated in methanol. Further purification of the product was achieved by dissolving the polymer in THF and reprecipitating it in methanol.

2.6. Synthesis of copolymer by electrochemical copolymerization

For the synthesis of conducting copolymer of PStPy, pyrrole was used as the comonomer. Polymerization was performed via constant potential electrolysis by using potentiostat and a three-compartment cell. A 1% (w/v) solution of insulating PStPy was dissolved in DM and both sides of Pt were coated with PStPy by drop-coating, and used as the working electrode. The electrolysis cell was prepared by dissolving TBAFB (0.1 M) in ACN and introducing 35 μL pyrrole. Constant potential electrolysis was performed at 1.1 V versus Ag/Ag$^+$ for 1 h at room temperature under inert atmosphere. The free standing films were washed in ACN to remove TBAFB after the electrolysis. Then films were kept in DM to remove ungrafted polymers.

For the spectroelectrochemical studies, P(PStPy-*co*-Py) copolymer was synthesized in the presence of 50 mg PStPy, 5 μL Py and a 0.1 M solution sodium perchlorate/lithium perchlorate in an ACN/DM (1:1 v/v) mixture at 1.1 V, in UV-cuvette equipped with ITO working and Pt counter electrodes with Ag/Ag$^+$ reference electrode via constant potential electrolysis. The electrochromic measurements, spectroelectrochemistry and switching studies of the polymer film deposited on ITO coated glass were performed in 0.1 M solution of NaClO$_4$/LiClO$_4$ in an ACN/DM (1:1 v/v) mixture in the absence of PStPy and Py.

3. Results and discussion

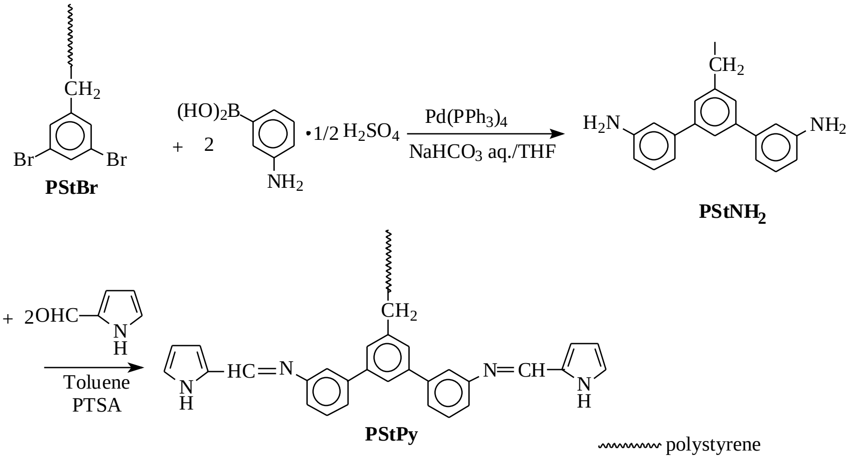
3.1. Synthesis of pyrrole functional polymer

Our strategy for the synthesis of a dipyrrolyl containing polystyrene was to start from a well-defined polymer synthesized by ATRP, which contains lateral aromatic dibrominated moieties. First modification of this polymer was attained by a Suzuki reaction using a commercially available low molecular weight boronic acid as coupling partner that gives the possibility for further modification (Scheme 2, PStNH$_2$).

The reaction between aryl halides and aryl boronic acids (Suzuki coupling) [33] is one of the most convenient methods for C–C coupling. We employed this method in the synthesis of polyphenylenes, in which a macromonomer having a 2,5-dibromo-1,4-phenylene moiety was reacted with an aromatic diboronic acid [23]. Macromonomers carrying boronic ester functionalities were also synthesized and used in Suzuki polycondensations in combination with aromatic dibromides. The reaction is quite simple and insensitive to moisture. Furthermore, this coupling reaction can be applied to monomers carrying functional groups [34,35].

The reaction conditions (high excess of boronic acid and long reaction times) were chosen so as to assure complete functionalization. Notably, the newly formed telechelics also contain a conjugated sequence (triarylene).

In the ^{1}H NMR spectra of the PStNH$_2$ (Fig. 1), the rests from the boronic acid could not be identified, as the aromatic protons



Scheme 2. Synthesis of PstPy.

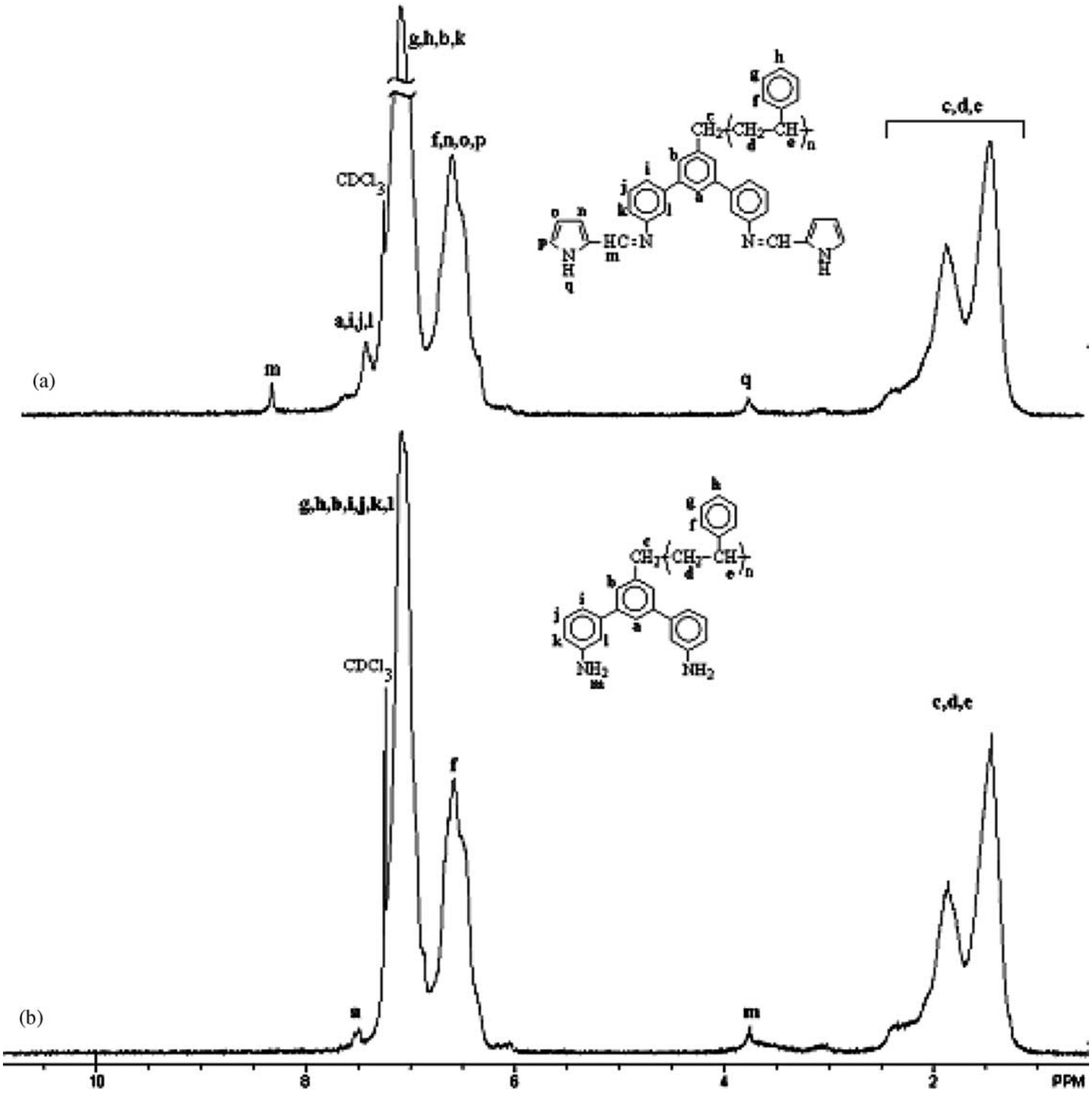


Fig. 1. ^{1}H NMR spectra of PSt functionalized polymers (a) PstPy and (b) PStNH$_2$.

originating from the St units give peaks in the same region. However, amino protons appear at 3.8–3.4 ppm as was confirmed by their disappearance with D$_2$O exchange. Additionally, the proton a, originating from the rest of ATRP initiator, is still visible.

FTIR spectrum of PStNH$_2$ displays usual PSt absorptions at 3058, 3025 cm^{-1} (aromatic CH stretching), 2970, 2851, 2848 cm^{-1} (aliphatic CH stretching), 1937, 1867, 1798, 1665 and 760 cm^{-1} (out-of-plane hydrogen deformation), 1598, 1489, 1446 cm^{-1} (in-plane-bend-stretching vibrations of phenyl ring), 758 and 697 cm^{-1} (out-of-plane hydrogen deformation). The peaks at 3456 and 3378 cm^{-1} are characteristic to the asymmetric and symmetric vibration modes of amino groups. The peak at 859 cm^{-1}, is attributed to the 1,3,5-trisubstitution of the benzene ring (Fig. 2(a)). Further functionalization of the PStNH$_2$ could be achieved by employing the amino groups in specific reactions. At the same time, this step can also be considered as a further evidence for the successful diamino-functionalization of the polymer, at the first stage.

The condensation reaction between aldehyde and amino derivatives with the formation of azomethine linkage (Schiff bases) is also an unpretentious organic reaction like Suzuki coupling, not sensitive to various other functional groups and nearly quantitative yields are often achieved if water is continuously removed from the reaction medium. On the other hand, fully aromatic polyazomethines have been known as an important class of thermally stable and highly conjugated materials. In recent years, a method was reported for synthesis of poly(Schiff bases) by cation-radical polymerization of conjugated monomers containing –CH=N– preformed groups and oxidizable groups at the extremities:

$$\text{Ox–CH} = \text{N–R–N} = \text{CH–Ox}$$

where R is an aromatic residue and Ox is an oxidizable group as 2-pyrrolyl, 2-thienyl or 1-naphthyl [36,37]. By chemical or electrochemical polymerization, polymers containing 2,2′-bipyrrolediyl or 2,2′-thienyldiyl rings or 1,1′-binaphthyl in the main chain, spaced by conjugated sequences containing azomethine units, are obtained. A similar approach has been

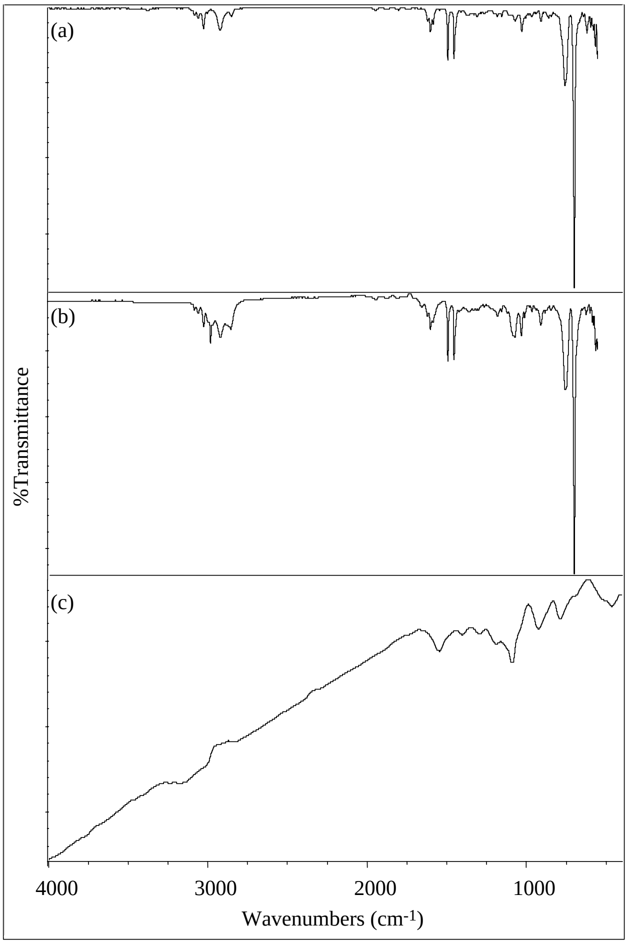


Fig. 2. FTIR spectra of (a) PStNH$_2$, (b) PstPy and (c) P(PStPy-*co*-Py).

applied in our case upon the reaction of amino telechelic PStNH$_2$ with 2-pyrrolyl aldehyde, a macromonomer having a fully conjugated sequence with oxidizable groups at the extremities was synthesized as shown in Scheme 2. In order to assure complete functionalization, a long reaction time was attained, with the use of high excess of low molecular weight compound.

In the ^{1}H NMR spectra of pyrrole functionalized type polymers (PStPy) (Fig. 1), peaks originating from pyrrole ring are covered by aromatic protons of the main polymer. On the other hand, the azomethine linkage proton gives a distinct signal at 8.32 ppm. The peak at 3.77 ppm was attributed to the –NH protons of pyrrole groups (**q**). A polymerization degree of about 22 for polymer 19 was calculated by comparing the integrals of **m** protons with the aromatic ones. The found value is close to that of the starting material (PStBr). This result also shows that a complete functionalization of the polymer was achieved. The clear signal of azomethine linkage is also a further proof for the presence of amino groups in the polymer PStNH$_2$.

The FTIR spectrum of PStPy exhibits new absorptions as compared with that of the starting PStNH$_2$ (Fig. 2(b)). The absorptions are at 3420 cm^{-1} (νNH), 1665 cm^{-1} (νC=N), 1417 cm^{-1} (ν pyrrole ring) and 879 cm^{-1} (β pyrrole ring) that confirms the H NMR results. After the potentiostatic copolymerization, a new peak at 1087 cm^{-1} revealed the presence of dopant ion, BF$_4^-$, and a peak at 1547 cm^{-1} stands for conjugation in the copolymer. The characteristic peaks of PSt at 758 and 697 cm^{-1} (out-of-plane hydrogen deformation), and the peak at 922 cm^{-1} belonging to 1,3,5 trisubstitution of the benzene ring were also existed in the FTIR spectrum of the conducting copolymer, P(PStPy-*co*-Py) (Fig. 2(c)).

3.2. Cyclic voltammetry

Oxidative electrochemical copolymerization of pyrrole functionalized polymer (PStPy) with pyrrole was carried out in acetonitrile (ACN)-tetrabutylammonium tetrafluoroborate (TBAFB) solvent electrolyte couple. Fig. 3 shows the anodic electrocopolymerization of a solution of PStPy with Py on a Pt-flake electrode by cyclic voltammetry at 500 mV s^{-1}. The redox process appears clearly at a relatively low potential of +0.20 V versus Ag/Ag$^+$.

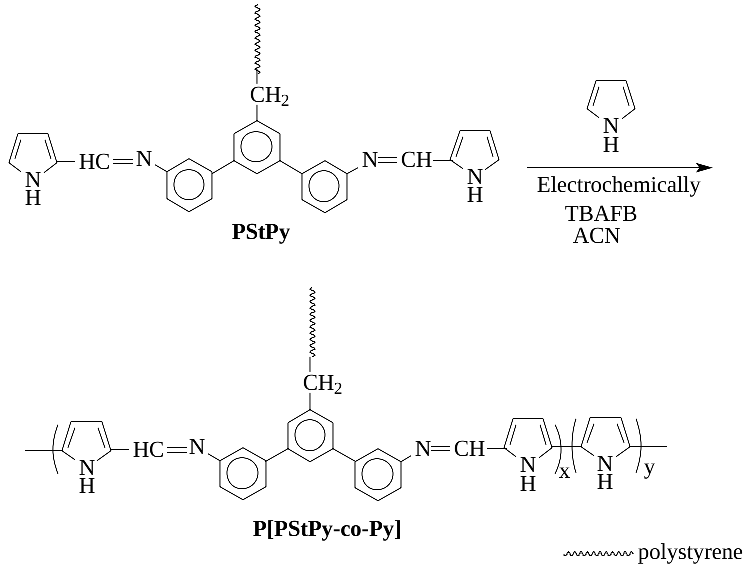
3.3. Electropolymerization of PStPy with Py

Polymer PStPy has a relatively long fully conjugated sequence terminated with oxidizable groups at the end of the chain. So, this polymer could readily be used in electrochemical oxidative copolymerization using pyrrole as comonomer yielding conducting polymers with macromolecular side chains (Scheme 3). As stated in Section 2, polymerization was performed via constant potential electrolysis by using potentiostat and a three-compartment cell.

3.4. Thermal behaviour

DSC thermograms of precusor polymer, copolymer, and Py were examined in the range 25–350 °C at a heating rate of 10 °C min^{-1} under N$_2$ atmosphere. DSC thermogram of

Fig. 3. Cyclic voltammogram of PStPy in the presence of Py at a scan rate of 500 mV s^{-1}.



Scheme 3. Electropolymerization of PStPy with Py.

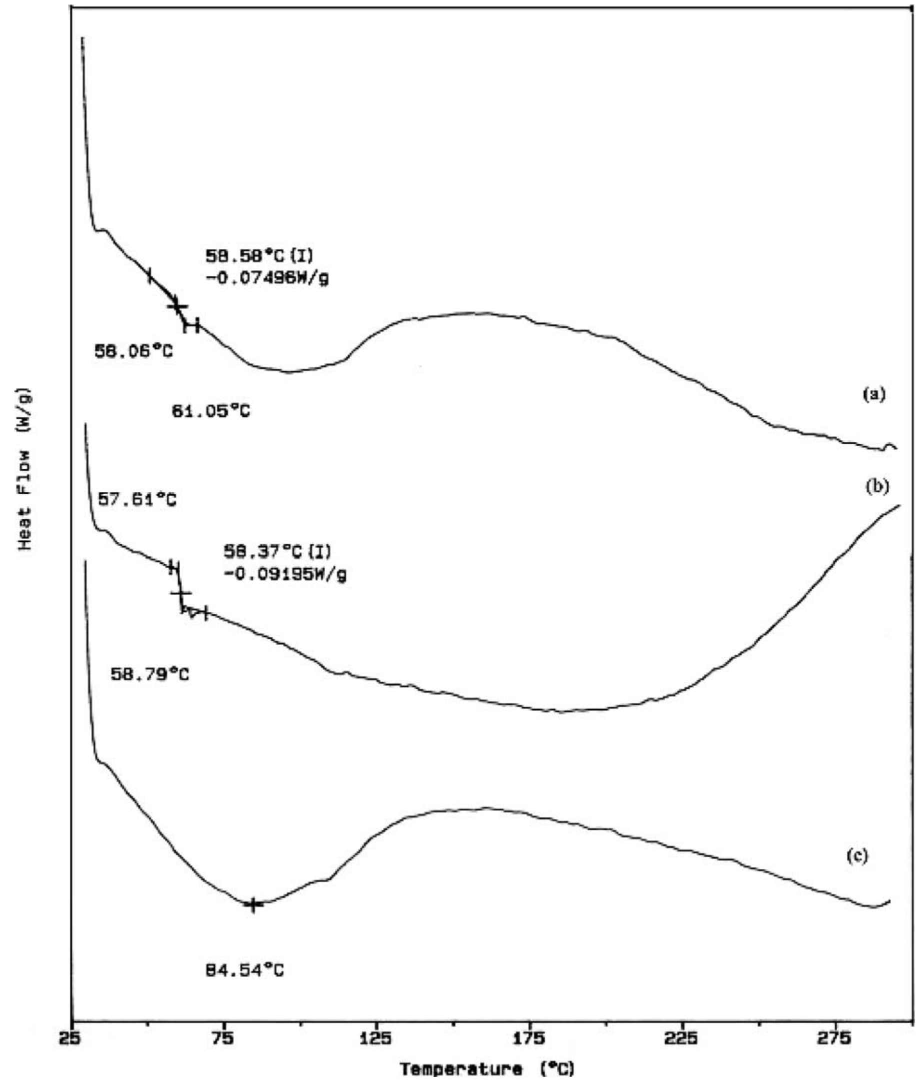


Fig. 4. DSC thermograms of (a) P(PStPy-*co*-Py), (b) PStPy, and (c) PPy.

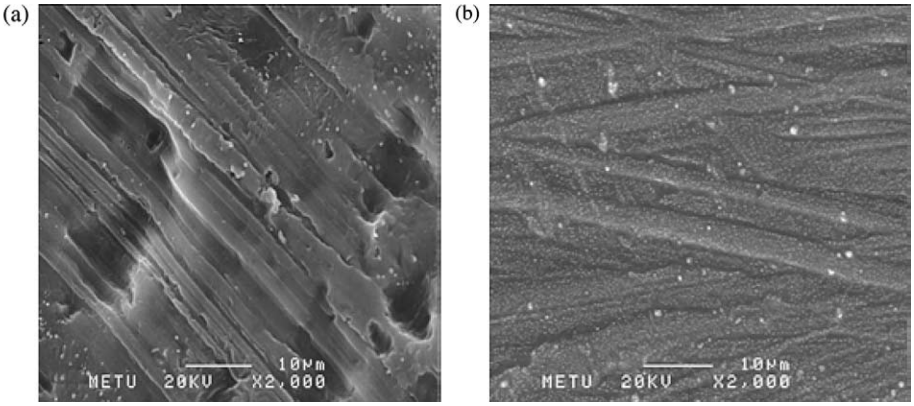


Fig. 5. SEM micrographs of (a) P(PStPy-*co*-Py), and (b) PPy (magnification 2000×).

PStPy, PPy showed glass transition temperatures (T_g) at 58.79 and 84.54 °C, respectively. DSC thermogram of P(PStPy-*co*-Py) indicated an endotherm at 58.58 °C (Fig. 4). DSC studies showed that thermal behavior of the copolymer is different from pure polypyrrole film, which is synthesized under the same conditions.

3.5. Morphologies of the films

Scanning electron microscopy (SEM) studies were carried out to investigate the morphologies of the films. Morphological comparisons of graft copolymer with corresponding pure PPy indicate the differences (Fig. 5). Electrode side of PPy, produced under the same conditions, is smooth whereas the copolymer reveals certain defects on the surface facing the electrode.

3.6. Spectroelectrochemistry of conducting copolymer

The P(PStPy-*co*-Py) film was deposited on ITO via potentiostatic electrochemical polymerization in the presence of 0.1 M solution of $NaClO_4$/$LiClO_4$ in an ACN/DM (1:1 v/v) mixture. As a result of the spectroelectrochemical analyses, both electronic structure of the copolymer and its optical behavior upon redox switching were clarified. The absorbance was recorded as a function of potential ranging from −0.7 to 0.6 V for P(PStPy-*co*-Py). The λ_{max} and the band gap energy values for the P(PStPy-*co*-Py) and PPy for the π–π^* transition were determined. P(PStPy-*co*-Py) has an absorbance at 393 nm (λ_{max}), and the band gap (E_g) was assigned as the onset of the π–π^* transition at 2.4 eV (Fig. 6(a)). The intensity of the π–π^* transition decreased while applied potential was increased, hence formation of charge carrier bands were observed. Upon stepwise increase of the applied potential from −0.7 to 0.6 V, alternation of the color from yellow to blue was recorded. Pure PPy has a peak absorbance at 357 nm (λ_{max}) and the band gap (E_g) was found to be 2.4 eV (Fig. 6(b)). These represent the differences between pristine PPy and the copolymers in terms of spectroelectrochemical behaviors, supporting copolymerization.

3.7. Electrochromic switching of copolymer

The electrochemical switching of P(PStPy-*co*-Py) was studied. The polymer films were synthesized on ITO-coated glass using constant potential. During the experiment, the % transmittance (T%) at the wavelength of maximum contrast was measured using a UV–vis spectrometer while the potential was stepped between −0.7 and 0.6 V for with a residence time

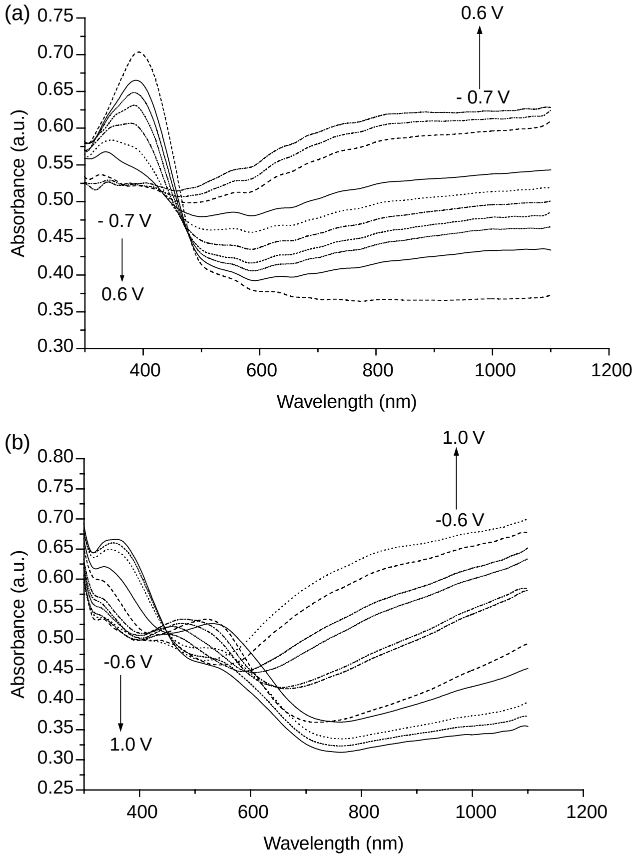


Fig. 6. Optoelectrochemical spectrum of (a) P(PStPy-*co*-Py) at applied potentials between −0.7 and +0.6 V in the presence of 0.1 mol/L solution of $NaClO_4$/$LiClO_4$ in an ACN/DM (1:1 v/v) mixture and (b) PPy at applied potentials between −0.6 and 1.0 V.

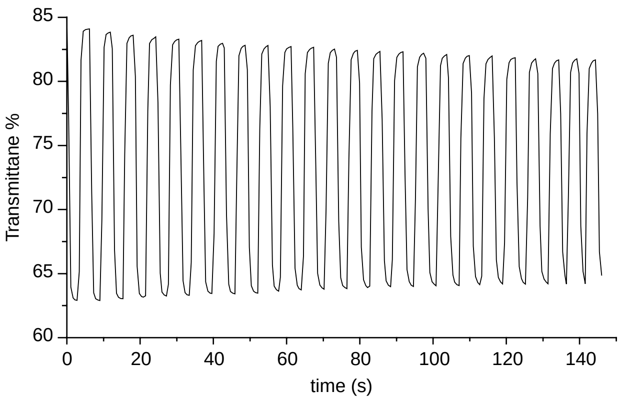


Fig. 7. Electrochromic switching, optical absorbance monitored for P(PStPy-*co*-Py) at 393 nm.

Table 1
Electrochromic properties

Materials	*l*	*a*	*b*
P(PStPy-*co*-Py)	Ox: 56	Ox: −2	Ox: −32
	Red: 88	Red: −13	Red: 76
PPy	Ox: 39	Ox: −4	Ox: −2
	Red: 28	Red: 40	Red: 8

Ox, oxidized state; Red, reduced state.

of 3 s. The optical contrast was measured as the difference between *T*% in the reduced and oxidized forms (%Δ*T*) and was found to be 20% for P(PStPy-*co*-Py) (Fig. 7). Results showed that the time required to reach 95% of the ultimate *T* was 1.7 s for the P(PStPy-*co*-Py). These values are comparable with the pristine polypyrrole sensitized by dyes [31,32].

3.8. Colorimetry

Accurate color measurements for electrochromic materials could be done by using CIE system that is used as a quantitative scale to define and compare colors. According to CIE color is made up of three attributes; luminance (*L*), hue (*a*), and saturation (*b*). Colorimetric measurements were performed using a Coloreye XTH spectrophotometer. The relative *L*, *a*, and *b* values of the copolymer were measured at the fully oxidized (blue) and reduced (yellow) states of P(PStPy-*co*-Py). The color of pure PPy turned from dark red to gray. *L*, *a*, and *b* values were given in Table 1.

4. Conclusion

A polymer containing a conjugated sequence having pyrollyl groups at the extremities was synthesized. The structure of PStPy was analyzed by spectral methods (^{1}H NMR, FTIR). The structure of the polymer contains oxidizable pyrrole groups enabling further electropolymerization. The syntheses of conducting copolymers of PStPy with pyrrole were achieved in the presence of the TBAFB as the supporting electrolyte. As a result, freestanding, stable and electrically conducting polymers were obtained. Characterizations of the resulting copolymer were performed by FTIR, SEM, spectroelectrochemical analysis, and electrochromic switching and colorimetry studies. Via spectroelectrochemistry studies for P(PStPy-*co*-Py), the observed band gap value was found to be 2.40 eV at 393 nm. The %Δ*T* were found to be 20% at 393 nm with the help of electrochromic switching studies. The results showed that the time required to reach 95% of the ultimate *T* was 1.7 s for the P(PStPy-*co*-Py).

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